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## **Measuring the effect of fuel chemical structure on particulate and gaseous emissions using isotope tracing**

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### **Abstract**

Using accelerator mass spectrometry (AMS), a technique initially developed for radiocarbon dating and recently applied to internal combustion engines, carbon atoms within specific fuel molecules can be labeled and followed in particulate or gaseous emissions. In addition to examining the effect of fuel chemical structure on emissions, the specific source of carbon for PM can be identified if an isotope label exists in the appropriate fuel source. Existing work has focused on diesel engines, but the samples (soot collected on quartz filters or combustion gases captured in bombs or bags) are readily collected from large industrial combustors as well.

### **Introduction**

Chemical pathways of combustion can be identified through tracing and measurement of unusual isotopes. Radioisotopes are specific and distinctive because they are extremely rare in natural materials. A radioisotope-labeled compound may have a very high abundance-to-background ratio, but poor signal-to-noise in the isotope detector may obscure this property. Detector sensitivity must increase as the radioactivity of the isotope of interest decreases. Short-lived radioisotopes can be efficiently detected by their decay but produce high radiation hazards in the laboratory. Radioisotopes with long half lives (e.g.,  $^{14}\text{C}$  half life = 5730 y) are inefficiently detected by measuring decays.

Rare stable isotopes can be used as tracers to avoid issues associated radioactivity but specificity of the label can be lost with the higher natural background. The rare stable isotope of carbon,  $^{13}\text{C}$ , occurs naturally at 1.1% while the natural abundance of  $^{14}\text{C}$  due to cosmic radiation is 1.2 parts in  $10^{12}$ . The ten orders of magnitude difference in natural background of these carbon isotopes significantly impacts ease of measuring an isotope signal. A one ppm concentration of a  $^{13}\text{C}$ -labelled compound (assume formula weight 200 g/mol) will change the  $^{13}\text{C}$  concentration by only 0.3 per 1000, measurable under good conditions using an excellent mass spectrometer. The same material labeled with  $^{14}\text{C}$  changes the concentration of that isotope in a contemporary biological sample by a factor of 3 million. Efficient detection of radioisotopes is a key to using this specificity.

Researchers in the mid-1980s labeled fuel components with  $^{14}\text{C}$  and traced the isotope to PM or soot from a diesel engine [1] or diffusion flame [1,2] using a decay-counting technique. These experiments required special radioactive test facilities to contain the large amounts of volatile radioactive compounds needed for decay counting and housing a radioactive engine. In addition to generating a significant amount of radioactive and mixed wastes, high level radioactive tracing can never be used in a realistic combustion environment.

An alternative technique to decay counting, accelerator mass spectrometry (AMS), is an isotope-ratio measurement method developed in the late 1970s as a powerful tool for tracing long-lived radioisotopes in chronometry in the earth sciences and archaeology [3]. The high sensitivity of AMS allows the specificity of the  $^{14}\text{C}$  atom to be used while avoiding radiological issues. Furthermore, AMS detection permits tracing with actual combustion systems in a realistic setting such as road vehicles in conventional dynamometer facilities. Samples prepared for  $^{14}\text{C}$  analysis are combusted to  $\text{CO}_2$  and then reduced to graphite for use in the AMS ion source. The technique counts individual nuclei rather than waiting for their radioactive decay, allowing measurement of more than 100  $^{14}\text{C}$  samples per day.

The contemporary quantity of  $^{14}\text{C}$  in living things (1.2 parts in  $10^{12}$  or 110 fmol  $^{14}\text{C}$ / g C) is highly elevated compared to the quantity of  $^{14}\text{C}$  in petroleum-derived products ( $< 1$  part in  $10^{15}$ ). Accordingly, components of bio-derived fuels contain elevated  $^{14}\text{C}$  as compared to fossil fuels. This isotopic elevation is sufficient to trace the fate of bio-derived fuel components in emission products without the use of radioactive materials. The most common substitutions are bio-diesel for fuel oil and bio-gas for natural gas. The complications of licensing and radioactive waste disposal are completely avoided by exploiting the sensitivity of AMS to measure the “non-radioactive” levels of  $^{14}\text{C}$  in bio-derived fuels.

Some petroleum-derived fuel components can be synthesized from biological sources. For example, long methyl esters (biodiesel) can be converted to paraffins that would then be uniformly labeled with the contemporary level of  $^{14}\text{C}$ . Obtaining sufficient fuel for use in a combustor by this synthesis method may be difficult, however. If synthesis of a fuel component from biologically-derived source material is not feasible, another approach is to purchase  $^{14}\text{C}$ -labeled material and dilute it with petroleum-derived material to yield a contemporary level of  $^{14}\text{C}$ . In each case, the virtual absence of  $^{14}\text{C}$  in petroleum-based fuels gives a very low  $^{14}\text{C}$  background that makes this approach to tracing fuel components practical.

If mechanisms of soot formation are understood, then combustion modeling can be used to evaluate possible changes in fuel formulation and suggest possible fuel components that can improve combustion and reduce PM and other emissions. The current combustion paradigm assumes that large molecules break down into small components and then build up again during soot formation. If all fuel components are broken down into 1- or 2-carbon species, then there should be little or no difference in the contribution of carbon from coal, polymers, aromatics, cyclo-alkanes, alkanes or oxygenated species in the PM emissions. AMS allows the labeling of specific carbon atoms within fuel components, tracing the carbon atoms, and testing this combustion modeling paradigm. The influence of neighboring atoms on the mechanisms by which a particular fuel molecule breaks into fragments can be studied. Furthermore, the propensity of specific molecular structures within fuel molecules (e.g., carbon-carbon double bonds, carbon-oxygen double bonds, carbon-hydroxyl structures) to form specific emission products can be measured.

Researchers at Southwest Research Institute (SwRI) showed that the addition of the oxygenate dimethoxymethane to diesel fuel not only reduced total PM emissions, but also increased the volatile organic fraction (VOF) of the PM [4,5]. The VOF of the PM can be oxidized with a catalyst in the exhaust stream to further decrease PM. A fuel formulation that significantly shifts PM to the VOF can be as valuable in reducing emissions as a variation that drops total PM but increases the non-volatile organic fraction (NVOF). AMS can be used to distinguish the  $^{14}\text{C}$  signal in the PM after it has been separated into

VOF and NVOF to help determine the chemical pathways by which fuel oxygenation affects PM composition.

The methods described below for tracing fuel components in the emissions of diesel engines can be applied to any combustion system. Any molecule containing carbon can be labeled with  $^{14}\text{C}$ . Although only recently applied to studies of engine combustion processes [6-10], the techniques for measuring the  $^{14}\text{C}$  concentrations of PM and  $\text{CO}_2$  by AMS are straightforward and routine.

## Facilities

Emission samples were collected from a fleet diesel engine at the University of California at Berkeley (UCB) and an optical research engine at Sandia National Laboratories (SNL). The facilities provide complimentary capabilities for collecting data and examining combustion mechanisms. Filter loading and gas collection is easily achieved from any industrial combustor using commercially available hardware. Existing stack sampling can be adapted by using appropriate filters and collection bags.

The UCB engine is a 1993 Cummins B5.9, a 6 cylinder 5.9 liter turbocharged and aftercooled diesel engine rated at 175 bhp. Fuel injection is achieved with a Bosch P7100 PE type inline pump capable of injection pressures of up to 115 MPa. No modifications were made to the engine or fuel injection system to optimize for operation on the test fuels. Fuel consumption was determined using a Micro Motion R025 coriolis flow meter. Modifications to the fuel return system were made to eliminate fuel return to the storage tank. The return line is instead routed back into the fuel delivery line and a shell-and-tube heat exchanger was installed to prevent overheating of the fuel in the short-circuited system. Gaseous emissions were monitored using Horiba gas analyzers as listed in Table 1. Measurements of PM were made via a mini-dilution tunnel designed and constructed at UCB (Fig. 1).

HC	Horiba Instruments FMA-220 flame ionization detector
$\text{CO}, \text{CO}_2$	Horiba Instruments AIA-220 infrared analyzer
$\text{NO}_x$	Horiba Instruments CLA-220 chemiluminescent analyzer

Table 1. Equipment for gaseous emissions measurements.

The SNL alternative fuels optical engine laboratory features a single-cylinder version of a modern-technology, Caterpillar 4-stroke direct injection (DI) diesel engine. This engine has been modified by SNL to provide extensive optical access into the combustion chamber as well as precise control of operating parameters [11,12]. The engine is based on the Caterpillar 3176/C-10 platform (350 bhp version) used in heavy-duty trucking, but utilizes a near-production HEUI-A fuel-injection system. In addition to standard cylinder-pressure-based diagnostic capabilities, windows in the upper periphery of the cylinder liner and in the piston crown enable in-cylinder combustion processes to be studied using advanced laser/imaging diagnostics.

The engine was operated in a skip-fired mode, with one combustion event every 12<sup>th</sup> engine cycle. The skip-fired operation mode was selected to reduce the risk of a window failure and to reduce ring wear because the upper piston ring pack is not lubricated. A 1200-rpm, moderate-load (8.00 bar gross indicated mean effective pressure) operating condition was studied, and injection timing was optimized such that the engine operated at peak efficiency.

The Center for AMS at LLNL houses three accelerators with different analysis capabilities [13-16]. The samples in this study were analyzed with the HVEE FN system operating at 6.5 MV (Fig. 2). All samples were prepared in the LLNL natural carbon prep lab using established methods [17]. The AMS

sample prep method accommodates samples containing between 0.05 and 10 mg carbon. Samples containing 0.2-2 mg carbon are preferred for obtaining higher measurement precision and lower systemic backgrounds. Approximately 15000  $^{14}\text{C}$ -AMS samples are measured annually at LLNL with 2-3 measurement days per week.

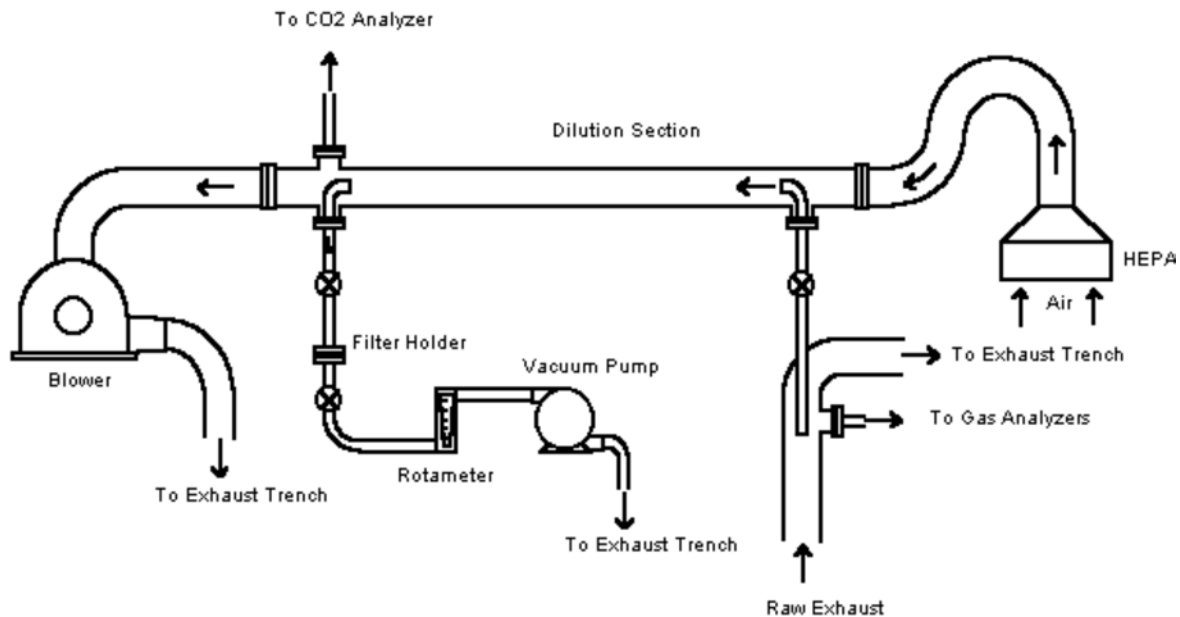


Figure 1. Schematic of UCB mini-dilution tunnel. Lines to the gas analyzers and diluted  $\text{CO}_2$  analyzer are shown. Gas sample for AMS analysis were collected in the line after the filter holder.

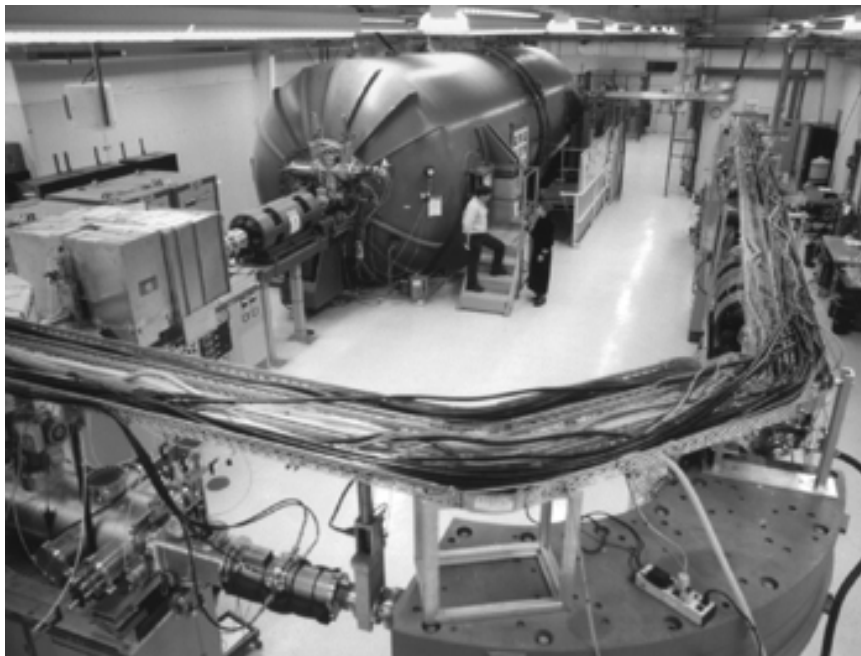


Figure 2: LLNL HVEE FN accelerator system viewed from the high energy end looking toward the ion source on the far side of the accelerator tank.

AMS is an isotope ratio mass spectrometry technique where  $^{14}\text{C}/^{13}\text{C}$  ratios of the unknowns are normalized to measurements of 4-6 identically prepared standards of known isotope concentration. Typical samples are placed in quartz combustion tubes with excess copper oxide (CuO), evacuated and combusted to  $\text{CO}_2$ . The evolved  $\text{CO}_2$  is purified, trapped, and converted to graphite in the presence of cobalt or iron catalyst in individual reactors [17]. Large  $\text{CO}_2$  samples ( $> 500\ \mu\text{g}$ ) can be split during graphite production for additional  $^{13}\text{C}$  measurement by stable isotope ratio mass spectrometry. The concentration of  $^{13}\text{C}$  can vary by 40 parts per 1000 between AMS samples, depending on the source of the carbon. Identified fuel components were measured for  $^{13}\text{C}$  and gave  $\delta^{13}\text{C}$  corrections of  $-27$  per 1000, values typical of fossil fuel. All graphite targets were measured at the Center for AMS at LLNL.

A cesium ion sputter-source is used to bombard the graphite samples and create a beam of negatively-charged carbon ions. Typical ion currents are 0.3-0.5 mA out of the source. Nitrogen does not form a negative ion so any potential interference from  $^{14}\text{N}$  is suppressed in the ion source. The low energy  $90^\circ$  magnet is set to select mass 14, charge  $-1$ , the mass and charge of our tracer ion. Since AMS is an isotope ratio technique, a fast pulsing mass separator is used to select the rare stable isotope of carbon,  $^{13}\text{C}$ , 1% of the operating time. The  $^{12}\text{C}^-$  component of the emitted ion beam is dumped into an off-axis Faraday cup.

The negatively charged ion beam is accelerated toward the terminal of the accelerator maintained at 6.5 MV. At the terminal (located in the center of the large tank in Fig. 3) is a thin carbon foil which is used to strip electrons off the incoming beam and change the charge of the ions. A distribution of charge states is obtained, with  $4+$  being the most plentiful under these operating conditions. The high charge state sees the high positive potential and is repelled out the high energy end of the accelerator, leaving the tank traveling at 32.5 MeV. Also, molecular isobars (e.g.,  $^{13}\text{CH}$  and  $^{12}\text{CH}_2$ ) that may have made it around the low energy magnet are unstable at the high charge positive charge state. The molecular fragments scatter into the walls of the instrument.

The high energy ion beam then passes through two  $90^\circ$  analyzing magnets which send the  $^{14}\text{C}$  beam along to the detector. The  $^{13}\text{C}$  selected by the mass separator is measured in an off-axis Faraday cup located between the magnets. A multiple-anode gas ionization detector containing 190 Torr of P-10 gas (10% methane, 90% argon) is used to measure energy loss of the incoming ions as they pass through the gas. The rate at which an ion loses energy depends on its charge, number of protons, and energy. These properties are used to differentiate between any nuclear isobars in the detector. The rate of energy loss in a single anode and the total energy of each incoming ion are used to set up regions of interest for specific ions. Although  $^{14}\text{C}$  does not have any interfering nuclear isobars, this detection method is used to separate any contamination from lithium-7, which occurs in some cases.

In addition to the magnets described above, the entire beam line contains electric and magnetic elements to focus the beam. Typical operating pressures are  $<10^{-6}$  Torr. The low pressures are important to minimize scattering of the ion beam. A general description of how AMS works is available in the literature [3].

## Materials and Methods

The  $^{14}\text{C}$  content of all major fuel components and lubrication oils must be measured prior to use in engines or other combustors. In our application, diesel fuel was not separated into components for individual measurements; its isotopic content was measured with the full additive and detergent commercial package added by the manufacturer. The extent of fuel measurement depends on the homogeneity of the fuel source (e.g. a municipal incinerator has a heterogeneous fuel supply that could be difficult to assess).

The fuels used in the UCB Cummins engine were baseline diesel fuel and blends of baseline diesel with different amounts of bio-derived ethanol to achieve the same total oxygen concentration. Table 2 lists fuel blends and  $^{14}\text{C}$  content of the major constituents in the UCB fuels. Because ethanol is soluble in diesel fuel in only small quantities, either an emulsifier (Span 85, i.e. sorbitan trioleate) or a cosolvent (n-butanol) was used to prepare the ethanol-in-diesel blends. An ignition improver, di-tert-butyl peroxide (DTBP), was also used to compensate for the low cetane number of ethanol and to give all blends the same cetane number (49.2) as the baseline diesel. The  $^{14}\text{C}$  content of this diesel fuel is higher than expected for a petroleum product. The addition of small amounts of contemporary carbon detergents are likely responsible for the elevation. The isotopic content of the lubrication oil was at instrument background. The contemporary carbon from the ethanol is the tracer in these fuels. Since the ethanol is bio-derived, it is uniformly labeled; each carbon atom in the ethanol molecule is equally labeled with  $^{14}\text{C}$ . The emulsifier is also derived from contemporary or renewable carbon.

Table 2. UCB test fuel blends (components listed in volume percent except for oxygen which is mass percent) and  $^{14}\text{C}$  content of components (amol  $^{14}\text{C}$ / mg C).

Fuel Component	Emulsified Blend	Cosolvent Blend	$^{14}\text{C}$ Content
Diesel	76.0	77.0	0.33
Ethanol	18.5	18.0	107
SPAN 85	4.0	-	110
n-butanol	-	3.5	0.09
DTBP	1.5	1.5	0.01
Oxygen	7.0	7.0	NA

For the SNL engine, the  $^{14}\text{C}$  concentration of all fuel components and the lubrication oil were checked by AMS and confirmed to be of petroleum origin ( $^{14}\text{C}/\text{C}$  ratios  $<10^{-15}$ ). The fuel used in this study was blended from an oxygenated hydrocarbon, dibutyl maleate (DBM) (see Fig. 3); a paraffinic hydrocarbon, n-hexadecane; and an ignition improver, 2-ethylhexyl nitrate. The ignition improver was required to achieve the desired ignition delay of 400  $\mu\text{s}$  under the current operating conditions (900 K and 60 bar at TDC when motored at 1200 rpm). The test fuel composition is provided in Table 3. The high concentration of DBM in the fuel was selected to study the combustion of the oxygenated hydrocarbon without the complication of high dilution in a conventional diesel fuel. Although the optical features of the engine were not directly exploited in these measurements, combustion of this fuel blend has been examined in detail at SNL [12]. A poly-isobutylene lubrication oil that cracked at  $\sim 570\text{K}$  was used so that any unburned lube oil deposited on filters during non-fired cycles could be easily removed from filters through heating.

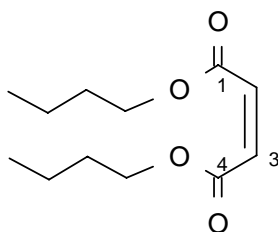


Figure 3: DBM molecule with the carbon atoms of the maleate numbered



Table 3: SNL test fuel with chemical components listed as volume percent.

Fuel Component	Volume %
Dibutyl maleate	88.0
n-hexadecane	7.0
2-ethylhexyl nitrate	5.0

Radiolabeled DBM was purchased from Moravsek Biochemicals, Inc. of Brea, CA. The [maleate-1,4- $^{14}\text{C}$ ]-DBM had a specific activity of 1 Curie/mol and was assayed at 98.6% radiochemical purity. The tracer  $^{14}\text{C}$  was located in the 1 and 4 carbon positions of the maleate (see Fig. 3). Several microliters of tracer were used to spike the fuel described in Table 3 and obtain fuel containing 90 fmol  $^{14}\text{C}$ /g C, approximately 85% the  $^{14}\text{C}$  found in living organisms.

All PM samples were collected on Gelman Sciences PALLFLEX tissuquartz 2500QAT-UP membrane filters. These quartz filters were pre-combusted at 1173 K for 3 h to remove all carbon residue and allowed to cool to 300 K in the furnace before removal.

Pre-combusted 47mm quartz filters were used for the PM measurements at UCB. Blank filters were first conditioned to ambient temperature and humidity overnight in petri dishes and then individually weighed with a Mettler UM 3 microbalance. Before sampling, the dilution ratio was adjusted to yield temperatures of the diluted exhaust below the required 325 K; resulting dilution ratios ranged between approximately 6 and 14 (See Fig. 1). The engine was operated at steady-state conditions of 1600 rpm and 285 N-m. Diluted exhaust was drawn through each filter for 10 minutes and the filters were then removed, placed in petri dishes and once again conditioned overnight before weighing. Four separate samples were taken for each point in the test matrix. A series blank was collected for each set of filters. Loaded filters are shown in Figure 4.

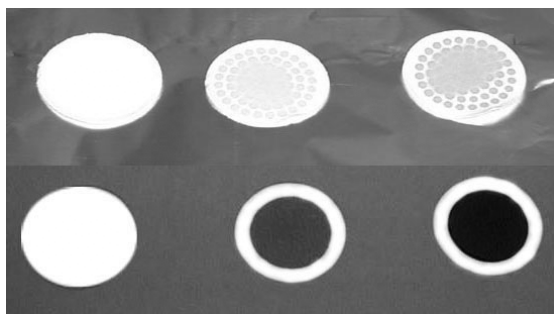


Figure 4. Filters loaded with PM from SNL (upper set) and UCB (lower set) engines. The SNL filters from left to right are a motored control, 48 fires in skip fire mode, and 96 fires in skip fire mode. The UCB filters from left to right are a blank control, a 25 minute collection with 20% ethanol, and a 10 minute collection with baseline diesel.

Within 24 h of pre-combustion, 37mm quartz filters were loaded with PM drawn from the exhaust manifold of the SNL optical engine (Fig. 4). When the engine was operated in skip-fired mode (fired every 12<sup>th</sup> cycle), a minimum of 72 fires were required to deposit sufficient soot for isotopic analysis. In practice, however, collecting PM over 216 fires produced a larger sample that was easier to process and analyze by AMS. Filters were handled with stainless steel forceps and placed on aluminum foil after

loading to avoid contamination with other carbon sources. Immediately after removal from the filter holder, each filter was transferred to a sealable plastic bag and placed in a dark opaque envelope. Several motored-only filters were also collected during each day of runs to ascertain the background from uncombusted lubrication oil collected on the filters during non-fired cycles. At the completion of the experiments for each day, the samples were taken to the natural carbon AMS prep lab at LLNL for processing.

For each fuel used at UCB, three gas samples were collected in 3.0 L Tedlar bags placed after the filter holder in the exhaust line. Each bag had a conventional fill valve and second septa seal port. The septa port was used to remove gas for AMS sample preparation. Gas samples were processed within several days of collection. The bags were maintained at temperatures between 290 and 300 K.

The diluted exhaust gases contained ~1% CO<sub>2</sub> and very low levels of CO. Approximately 40 mL of exhaust gas at atmospheric pressure was transferred to an evacuated stainless steel AMS graphitization line. The transfer volume was selected to produce an AMS sample containing approximately 1 mg carbon. Water, sulfur dioxide, and unburned fuel were removed using a dry ice-isopropanol cold trap. The CO<sub>2</sub> was then cryogenically condensed in a liquid nitrogen cold trap and non-condensable gases (NO<sub>x</sub>) were removed. The CO<sub>2</sub> was then moved to a graphitization head [17] for conversion to an AMS graphite sample.

Gas samples were collected in 10 L Tedlar bags for the SNL engine also located after the filter housing and an oil-free diaphragm pump. The bags were filled over a 72 fire cycle. Since the engine is skip fired, most of the gas in the bag is intake air. The entire volume of the bag was processed to obtain ~10 mg C as CO<sub>2</sub>. Aliquots were taken to obtain AMS samples in the 1-2 mg C range. A detailed description of the gas separation technique is in the literature [10].

Beyond measuring total PM emissions, we sought to determine partitioning of the PM. In practice, the criteria for this separation are operationally defined by the investigator. Depending on the field of the investigator, the separation of PM carbon is commonly described by the following pairs: elemental and organic carbon, soluble organic fraction (SOF) and insoluble organic fraction (IOF), or volatile organic fraction (VOF) and non-volatile organic fraction (NVOF). We prefer the VOF/NVOF nomenclature because it reflects the process we use and the physical properties employed in any realistic exhaust treatment scheme.

Loaded filters were cut in half with a clean stainless steel surgical scissors. One half was cut into strips and placed in a quartz combustion tube with CuO oxidizer to combust to CO<sub>2</sub>. The combusted sample was then converted to an AMS graphite sample [17]. These samples are measurements of the total carbon in the PM. The other half filter was heated to 613K for 2 h in a furnace and then allowed to cool to room temperature to remove the VOF. The VOF is estimated by measuring the difference in mass of the two half filters. This procedure to remove the VOF was developed to obtain consistent isotope ratios and mass fraction of the NVOF from National Institute of Standards and Technology (NIST) standard reference material (SRM). NIST SRM 2975 (diesel soot) and SRM 1649a (urban dust) are the closest NIST SRMs to exhaust PM. The filters loaded with PM lose mass during the thermal separation and the soot deposits are noticeably lighter in color. The remaining carbon is the NVOF. The filters with NVOF are then prepared as AMS samples with the usual procedure [17].

Traditional gravimetric measurements of filters can be misleading for several reasons. It is difficult to measure 100 µg variations in a 100 mg filter. Furthermore, the filters are fragile and it is easy to lose small pieces on the soot-free border when handling with forceps. The PM deposited on quartz filters has very high specific surface area and readily absorbs water and other molecules from the vapor phase. An

alternative technique for quantifying carbon utilizes the CO<sub>2</sub> pressure from the completely combusted sample measured during the AMS graphite preparation method.

AMS is an isotope ratio mass spectrometry technique where <sup>14</sup>C/<sup>13</sup>C ratios of the unknowns are normalized to measurements of 4-6 identically prepared oxalic acid standards of known isotope concentration. The standard is a NIST certified Contemporary Standard for Carbon-14 Dating Laboratories.

The measured ratio of <sup>14</sup>C to total C for each sample ( $R_{sample}$ ) is described below. The concentration of the <sup>14</sup>C labeled fuel component is  $^{14}C_{tracer}/C_{tracer}$ . The contributions from the fuel and additives to the measured ratio are  $^{14}C_{fuel}/C_{fuel}$  and  $^{14}C_{add}/C_{add}$ , respectively. The background contribution is  $^{14}C_{bk}/C_{bk}$  and the possibility of contamination to the sample is indicated as  $^{14}C_{uk}/C_{uk}$ .

$$R_{sample} = \frac{^{14}C_{tracer} + ^{14}C_{fuel} + ^{14}C_{add} + ^{14}C_{bk} + ^{14}C_{uk}}{C_{tracer} + C_{fuel} + C_{add} + C_{bk} + C_{uk}} \quad (1)$$

In theory, all the components in (1) need to be determined by a series of control experiments. In practice some components can be minimized by experimental design. In the case of PM samples, the <sup>14</sup>C terms of petroleum derived fuel components are insignificant, only a biologically-derived additive (e.g., SPAN 85) contributes to the <sup>14</sup>C content. The  $^{14}C_{bk}$  component is a systemic background of ambient CO<sub>2</sub> absorbed by the deposited PM. It is hoped that  $C_{uk}$  is eliminated and  $C_{bk}$  is consistently measured in blanks and baseline diesel samples.

The isotope ratio of the sample,  $R_{sample}$ , is calculated from the measured isotope ratios of the sample,  $R_{sample(meas)}$ , the average of the measured standards,  $R_{stand(meas)}$ , and the known isotope ratio of the standard,  $R_{stand}$  shown in (2).

$$R_{sample} = \frac{R_{sample(meas)}}{R_{stand(meas)}} R_{stand} \quad (2)$$

Traditional tracer experiments generally depend on radioactive decay and are dominated by a highly labeled tracer with very small mass. In our case, the tracer contributed a significant amount of carbon to the measured isotope ratio. The denominator of (1) is an expression for the total carbon mass of the sample. The product of the isotope ratio and carbon mass is the quantity of <sup>14</sup>C in the sample. The <sup>14</sup>C in the measured sample comes from the fuel components, whose isotope ratios we measure. The relative contribution of the tracer to the PM <sup>14</sup>C content can then be calculated by subtracting the sum of the contributions of the non-tracer fuel components from the total <sup>14</sup>C in the sample. The carbon mass of the tracer,  $C_{tracer}$ , in the PM is determined by dividing the tracer <sup>14</sup>C content,  $^{14}C_{tracer}$ , by the tracer <sup>14</sup>C concentration,  $R_{tracer}$ , as in (3).

$$C_{tracer} = \frac{^{14}C_{tracer}}{R_{tracer}} \quad (3)$$

The fraction of PM mass attributable to the tracer,  $F_{tracer}$ , is then the ratio of  $C_{tracer}$  to sample carbon mass,  $C_{sample}$ , as shown in (4).

$$F_{tracer} = \frac{C_{tracer}}{C_{sample}} \quad (4)$$

## RESULTS AND DISCUSSION

All filters collected contained sufficient carbon to produce adequate samples for analyses. In general, the UCB fleet engine operating with conventional dilution tunnel and gas analyzer technology produced large PM samples that were easy to analyze. The SNL optical engine operating in skip-fired mode produced much less PM.

The baseline diesel, homogeneous cosolvent and heterogeneous emulsified blends produced very different emissions. Combustion modeling did not predict these differences because the chemical kinetic models do not account for the heterogeneity of the fuel. The homogeneous cosolvent blend (described in Table 2) reduced total PM emissions to 71% of the baseline diesel level while the heterogeneous emulsified blend actually experienced a 14% increase in total PM mass measured gravimetrically. The carbon mass in the PM generated from the cosolvent and emulsified blends was almost identical when measured from CO<sub>2</sub> pressure during AMS sample graphitization. NO<sub>x</sub> emissions from the ethanol-in-diesel blends were 89% that of the baseline diesel for both blends, probably due to lower combustion temperature. Emissions of both HC and CO increased, but remained very low as is typical with diesel engine combustion. With our fixed load operation, fuel consumption was higher with the test fuel blends due to the lower energy density of ethanol.

The CO<sub>2</sub> pressures measured from half filters during the production of graphite for AMS analysis provide an accurate measure of carbon mass. The partitioning of carbon in the VOF and NVOF for the different fuel is shown in Figure 5. The baseline diesel and cosolvent blend both have roughly 55% VOF in this trial. The emulsified blend had a much larger more variable VOF, 75-90%.

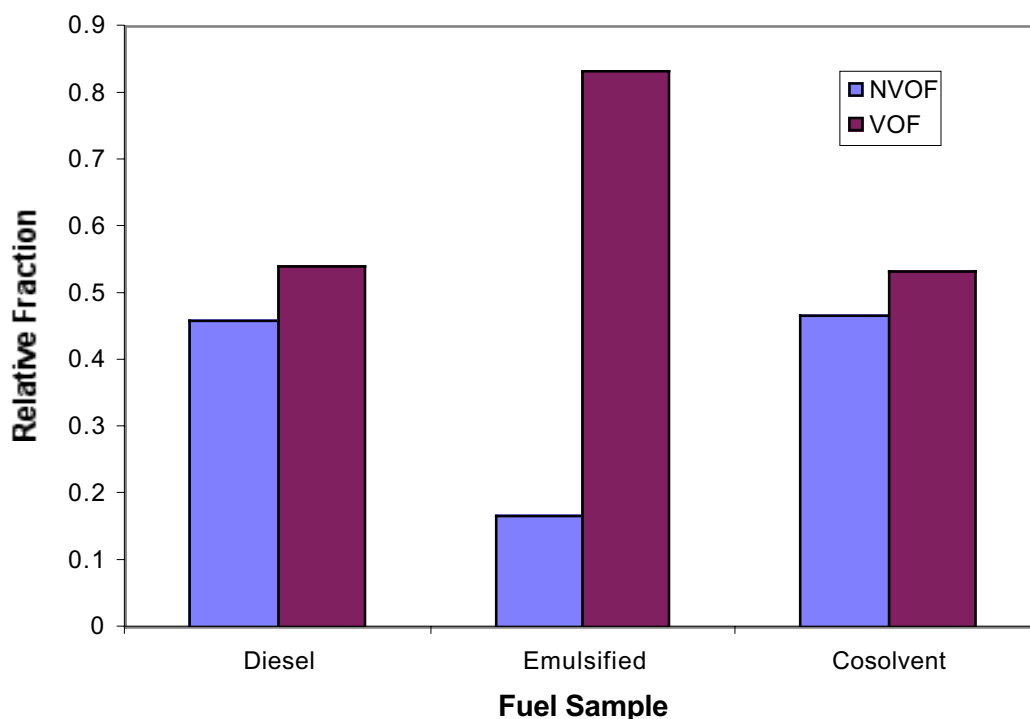


Figure 5. Partitioning of PM carbon between VOF and NVOF on filters loaded with baseline diesel, emulsified blend and cosolvent blend fuels. Baseline diesel VOF/NVOF partitioning varied by ~2% among replicate samples. The emulsified blend experienced much larger variations of ~10%.

When viewed in conjunction with the brake-specific emissions, the large VOF of the emulsified blend yields a brake-specific PM NVOF only 23% that of diesel assuming 80% VOF from the emulsified blend. The cosolvent blend yields a brake-specific PM NVOF 32% that of diesel assuming 55% VOF partition. The NVOF PM is more resistant to exhaust oxidation, so driving more PM into the VOF may be more effective than simple PM mass reduction in reducing emissions.

The  $^{14}\text{C}$  content of the ethanol provides the tracer for determining the fate of the ethanol-derived carbon in the engine emissions. The  $^{14}\text{C}$  signal from the bio-derived ethanol in the PM was easily measured above the isotope level of the baseline diesel. Blank filters used to measure the carbon mass and isotopic content of the ambient environment absorbed approximately 25  $\mu\text{g}$  carbon with a  $^{14}\text{C}$  content about 50% of bio-derived plants. In a half filter this background accounted for 0.5 amol of  $^{14}\text{C}$ . Filters loaded with PM from running baseline diesel also absorbed approximately 0.4 amol of  $^{14}\text{C}$  between loading and AMS sample processing. Since fresh soot is more absorbent than aged soot, it is reasonable to assume most of this  $^{14}\text{C}$  was absorbed in the engine lab where the ambient  $^{14}\text{C}$  content is 50% that of contemporary plants as measured from blank filters. This absorbed mass is approximately 10  $\mu\text{g}$ . Finally, the  $^{14}\text{C}$  content of the diesel fuel is 0.3 amol  $^{14}\text{C}$  / mg C. This level is higher than expected for a petroleum-derived material. Commercial diesel fuel contains a variety of additives, some of which may have bio-derived carbon, that slightly elevate the  $^{14}\text{C}$  above a single petroleum derived molecule (e.g. n-butanol in this study). The PM collected from the baseline diesel fuels contained about 1.2 amol  $^{14}\text{C}$  / mg C. The thermal treatment to remove the VOF cut this background level to 0.7 amol  $^{14}\text{C}$  / mg C.

Several trends were observed among the samples analyzed for  $^{14}\text{C}$  content of total carbon PM. The total carbon PM for the cosolvent blend had a lower  $^{14}\text{C}$  concentration than that of the emulsified blend. Compared to the isotope content of the  $\text{CO}_2$  from each fuel, the cosolvent blend produced PM with a  $^{14}\text{C}$  concentration ~35% that of the  $\text{CO}_2$  while the emulsified blend produced PM with a  $^{14}\text{C}$  concentration ~40-45% that of the  $\text{CO}_2$ . The carbon mass generated by cosolvent and emulsified blends were almost identical.

The trend that ethanol-derived carbon was less likely than diesel fuel-derived carbon to be found in the PM is not surprising. If the difference between  $\text{CO}_2$  and PM partitioning were due only to the stability of the C-O bond in the ethanol, the reduction in PM  $^{14}\text{C}$  content would likely be closer to 50%: the carbon attached to the oxygen would all be oxidized to  $\text{CO}_2$  while the other carbon would behave like the diesel-derived carbon. Since the difference is greater, the carbon not adjacent to the oxygen in ethanol does not combust like the diesel fuel. It may be preferentially oxidized to  $\text{CO}_2$  or there may be a significant contribution of ethanol-derived carbon in small volatile aldehydes formed during combustion. Techniques to separate and measure isotopic content of semi-volatile compounds are being investigated. The contemporary emulsifier could not entirely account for the higher  $^{14}\text{C}$  content of the emulsified blend PM.

Carbon mass measured by  $\text{CO}_2$  pressure from combusted half filters was the same for cosolvent and emulsified blends. The emulsified blend produced PM with higher mass but did not contain more carbon. Furthermore, much of this larger mass was volatile. The combination of no carbon and volatility of the PM, and the possibility of unburned emulsifier in the PM suggest that the higher PM mass may be due to absorbed water.

For the cosolvent blend, 63-87% of the ethanol-derived carbon in the PM resided in the NVOF. In the case of the cosolvent blend, it appears that the ethanol-derived carbon resides primarily in the building blocks of soot rather than in condensed volatiles on the surface of the PM. The tendency of ethanol to produce acetylene and other soot precursors during combustion is supported by this data. For the emulsified blend, 20-35% of the  $^{14}\text{C}$  in the PM resided in the NVOF. Some of the loss of  $^{14}\text{C}$  to the VOF

for the emulsified blend appears to be associated with the emulsifier. Control experiments in which emulsifier was added to diesel without ethanol indicated that emulsifier-derived carbon resided mostly in the VOF.

Since the majority of the carbon from the fuel is fully combusted, the isotope ratio of the collected  $\text{CO}_2$  reflects the isotopic content of the fuel. The  $\text{CO}_2$  from the emulsified blend has more  $^{14}\text{C}$  than the cosolvent blend as expected due to use of a contemporary emulsifier. The  $\text{CO}_2$  contained 17 amol  $^{14}\text{C}/\text{g C}$  and 13 amol  $^{14}\text{C}/\text{g C}$ , mirroring the isotopic content of the emulsified and cosolvent UCB fuels.

All filters from the SNL experiments were loaded with a significant amount of carbon. Unfortunately, much of it was unburned lubrication oil. The lube oil deposition decreased over the course of a day, but the total carbon remained significant on filters collected with motored cycles only. Using the polyisobutylene lubrication oil with the low cracking temperature ( $\sim 570\text{K}$ ) removed the large carbon background on the filters. The motored only filters had insufficient carbon ( $0\text{--}5\ \mu\text{g}$ ) to produce an AMS sample. The heating procedure to remove the VOF did not visibly reduce the deposited soot.

The  $^{14}\text{C}$  content of the motored and skip-fired PM samples was almost identical and 3 orders of magnitude smaller than the bulk fuel, indicating that effectively all of the labeled carbon in the DBM was combusted to  $\text{CO}_2$  that passed through the PM collection filter (Fig. 6).

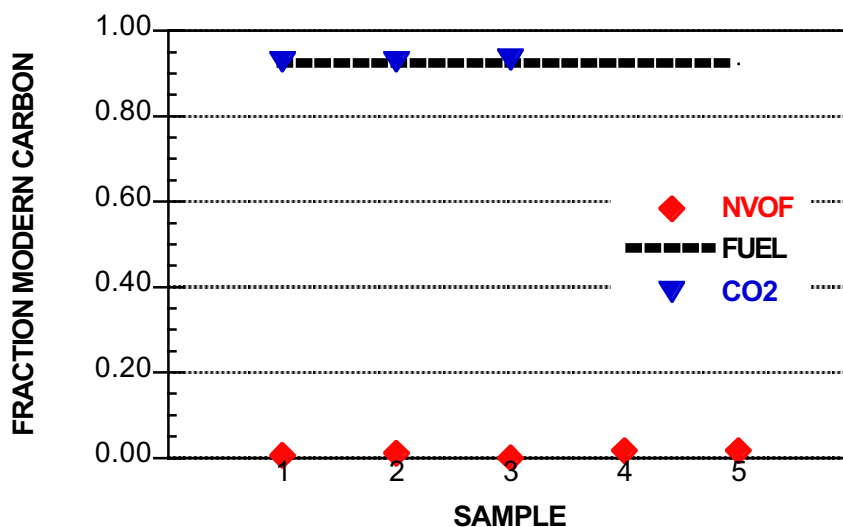


Figure 6. Carbon-14 content of the fuel, NVOF PM, and  $\text{CO}_2$  from 1,4 maleate label DBM. Fraction modern carbon is the concentration of  $^{14}\text{C}$  relative to the modern level in living tissue, roughly 100 amol  $^{14}\text{C}/\text{mg C}$ .

The absence of  $^{14}\text{C}$  from the filters in general (and from the PM in particular) indicates that the labeled carbon atom in the DBM, the 1,4 maleate position, is thoroughly oxidized to  $\text{CO}_2$  (see Fig. 3). We are proceeding to repeat these runs with  $^{14}\text{C}$  labels on different carbon atoms in the DBM. The 2,3 maleate position is particularly interesting. There is a double bond between the 2 and 3 carbon positions in the maleate, a structure likely to produce soot precursors. Carbon atoms in the butyl group can also be labeled with  $^{14}\text{C}$ . By selectively labeling specific carbon atoms in a fuel, the tendency of neighboring atoms to influence the sites of molecular cleavage during combustion can be interrogated. The

deposition of the tracer into different emission products depends upon the molecular fragments formed during combustion. This type of data can help combustion modelers construct and refine chemical-kinetic combustion mechanisms.

## CONCLUSION

AMS provides a means of following the fate of carbon in specific compounds from the fuel to the emissions from any combustion source. Selective labeling of specific carbon atoms within a fuel component provides direct experimental evidence of the behavior of different chemical groups during combustion. In addition to providing data validation to combustion modelers, the data provides insights into which chemical structures within fuels and additives most greatly influence emissions.

The almost complete lack of  $^{14}\text{C}$  in the PM collected with the DBM fuel labeled in the 1,4 maleate position suggests that the carbon-oxygen double bond does not break during combustion. Experiments designed to examine the influence of neighboring atoms on the carbon atoms in other chemical structures are underway.

The ease of using the contemporary tracer carbon in ethanol demonstrated the simple application to tracing bio-derived components of blended fuels. Although the majority of the ethanol-derived carbon was fully oxidized, more ethanol-derived carbon appeared in the PM than one might expect for a molecule containing so much oxygen. The data points to potential problems of using oxygenates which form unsaturated  $\text{C}_2$  fragments during combustion. The differences in the PM produced with cosolvent and emulsified blends suggests that the distribution of oxygen in the fuel, not just its content, significantly affects PM production.

The extension of carbon isotope tracer analysis from engines to industrial combustors is straightforward. Methods for analyzing PM and  $\text{CO}_2$  are well established. Sample size limitations in engines should not be a problem for larger combustors, so the analysis of less common chemical species in emissions should be easier. Basic chemical separation techniques could be implemented to isolate and analyze CO, small acids (e.g., formic and acetic) and aldehydes produced in combustion. Measuring these products can validate and improve combustion models and provide information on the effectiveness of combustors and emission control devices. AMS enables carbon isotope tracing in actual systems without the complications of radioactive materials.

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